THE PLASTOFROST TECHNIQUE FOR STUDYING THE CARBONIZATION OF COAL - A RE-EXAMINATION

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Introduction

The Plastofrost technique was developed by Ritter and Juranek[1,2] in West Germany to observe the coal-to-coke transformation (softening, pore development and resolidification), and the interaction of coal macerals at different degrees of carbonization. Changes occurring at different temperatures during the process become visible and if captured on film, produce a time-temperature record of the carbonization stages. Although hailed as a useful technique by researchers the Plastofrost technique enjoyed just a brief period of popularity. Since the 1960's the technique does not appear to have been mentioned in the coal science literature. A recent thesis[3] seems to have rekindled interest in the method.

Our objectives in this paper are to describe the Plastofrost technique and the modifications we have made, illustrate the information obtained, and to examine the range of scientific and technical questions this procedure can be used on.

The principle of the Plastofrost technique is to produce a temperature difference across a coal sample so that the bottom of the sample reaches at least 550°C when the top of the sample has not yet attained 350°C. The maximum temperature ensures that semicoke forms so that the coke texture can be observed, while limiting the top temperature permits dewatering to occur, but not softening. Placing thermocouples in the sample gives the temperature gradient; the temperature at each point in the sample is known and a temperature can be assigned to each visible stage of the coal to coke transformation. Heating of the sample is unidirectional just as in a coke oven. However, in the Plastofrost unit, the sample is heated from the bottom. It differs, therefore, from a coke oven in the direction of gas flow with respect to the temperature front. Some of the gas in a coke oven will move through the hot zone, and undergo further cracking, whereas in the Plastofrost, gas flow is only into the cooler region of the sample. The significance of this difference is not known. Nevertheless, movement of the temperature front through the sample makes the Plastofrost a better model of a cake oven than a dilatometer or a plastometer whose designs emphasize uniform heating.

Equipment

Figure 1 shows a schematic (elevation) of the Plastofrost apparatus as modified for the present study. The two main components are the furnace and the coking attachment. The furnace consists of a nickel-plated copper slab in which four 300 watt cartridge heaters are enclosed. A chromel/alumel thermocouple insulated with ceramic tubing placed 5 mm beneath the top surface of the slab measures the temperature (see Fig. 1). The bead of the TC is at the centre of the slab.

The coking attachment comprises a baseplate; a coking cylinder; and a ram. The coking cylinder has an inside diameter of 41 mm and a height of 75 mm. Wall thickness is 3 mm. The cylinder can be separated vertically into halves and has ten evenly spaced holes 5 mm centers, along each side of the vertical split. Ceramic tubes (2.5 mm o.d.) are placed in these holes, as shown in Figure 1, and chromel/alumel thermocouples are inserted so that the measuring junctions are located along the axis of the cylinder. Halves

of the cylinder are clamped together as shown in the figure.

The cylinder fits into an insert in the baseplate. This plate measures 110 mm x 110 mm and is 6 mm in thickness (Fig. 1). Three 6.3 mm rods, 115 mm in height extend from the base plate to the retainer for the ram. The ram itself is 10 mm thick and has a diameter of 39.75 cm, just slightly less than the inside diameter of the coking cylinder so that it can easily compact and retain the coal within the cylinder. It is fitted with a 76.5 cm long "T-shaped" handle, threaded through the retainer. Thus the ram can be raised or lowered to provide any desired degree of compaction in the coal.

The coking attachment is placed in a snug fitting inset on the top plate of the furnace. This is stepped as shown in the figure to reduce heat flow to the cylinder walls. The furnace provides unidirectional heating to the sample in the cylinder from the bottom upwards.

A microcomputer based control and data acquisition system is required to monitor the 10 thermocouples in the sample and to control the furnace temperature. Details are given by Duever [3] and in a WCPD report [4].

Procedure

Prior to loading, an aluminum foil was placed in the coking cylinder and ceramic tubes, 5 cm in length, were fitted in to the holes located in the coking cylinder. The cylinder was placed on the baseplate before coal was added. A sample of air dried, ground coal, weighing 85 grams, was incrementally packed into the cylinder using the ram to guarantee a constant packing density of 0.9 g/cm^3 for all samples. The attachment was then suitably insulated using fibrefax and insulating tape. Insulation was needed to ensure a uniform radial temperature distribution. The ten chromel/alumel thermocouples were inserted into the ceramic tubes and connected to a junction strip as the last step. In some experiments, only 66.5 g of coal were used to give a density of 0.76 g/cm^3

The samples were heated in air until the temperature in the lowest level of the coal reached 200°C. At that time nitrogen was introduced into the test chamber to prevent oxidation of the sample. The furnace was heated thereafter at the maximum heating rate until its temperature reached 400°C. The temperature in the lowest level of the packed coal sample at this time was usually about 250°C. Above 400°C the furnace heating rate was controlled at 3°C/min. Heating continued until the temperature in the lowest level of the coal reached about 550°C. At this time, the furnace was turned off, the coking apparatus removed from the furnace plate left to cool in an inert atmosphere until the temperature at all levels fell below 200°C. At this point, the foil wrapped sample was impregnated using a polyester resin sometimes thinned with acetone. After hardening the sample was cut into two pieces perpendicular to the ceramic tubes using a diamond-tipped circular saw. Each half was impregnated with polyester resin again, but this time under vacuum.

The final step in sample preparation was grinding and polishing. The former followed the recommendations of the Bituminous Coal Research Inc. [5]. The exposed face of the coked samples were polished to produce scratch-free surfaces suitable for microscopic examination using three polishing stages, each of three minutes duration. After each polishing stage, an ultrasonic cleaner was used to remove all polishing or grinding particles. Using a Zeiss UNIVERSAL Research Microscope, Plastofrost samples were examined by reflected light using parallel polars and a 1/4 λ plate inserted between the specimen surface and the analyzer to characterize the samples in terms of their optical texture. A strip 5 mm wide on either side of the center axis of the cylinder was examined. Juranek et al. [6] measured the temperature profile perpendicular to the center axis and found that within such a strip, deviation from the temperature along the center axis was within 3°C.

The first step in the microscopic evaluation was to determine the relative positions of the ceramic tubes making use of a stage micrometer. These tubes held the thermocouples during the tests so that the exact temperatures at these positions were known. Then samples were examined at 50X magnification in air to observe the softening characteristics of the coal, its resolidification, and the nature of the coke formed. This was accomplished by identifying the following transitions found by Ritter and Juranek [1,2] and Juronek [6] to be common to coking goals.

1) The first appearance of pores in the individual grains.
2) The initial fusion of the grains.
3) The point at which there is a significant increase in the proportion of pores.
4) The completion of fusion where individual grains are no longer distinguishable.
5) The development of anisotropic semicoke.

With the aid of the stage micrometer, positions could be assigned to each of these changes to the nearest tenth of a millimeter and the temperatures for each transition could be estimated from the temperature record.

Completion of fusion and a significant increase in pores are relatively gross characteristics and could easily be identified at 50X magnification. Determinations of initial pore development and grain fusion were more difficult and generally required higher magnifications of 100 and 200X. The anisotropic nature of the semicoke was observed at 200 and 500X magnification. The development of anisotropy in the softened coal mass is an indication of decreasing viscosity. With increasing time and temperature, anisotropic domains grow and may form large regions of uniform orientation. Thus since these domains should not change above the resolidification point, the point at which domains cease to grow and change should be the resolidification temperature.

Further details of procedure are available [3,4]. Several experiments were performed using coal-bitumen slurries. A different procedure had to be developed to prepare samples from slurries. Fluidity of the slurry during heating was a problem. A paper at recent ACS Symposium [7] discusses the procedure developed. An extended discussion appears in a report in the public domain [10].

Plastofrost Observations

As mentioned above, some of the carbonization stages are easily identified. One of these is the completion of fusion. Figure 2 shows the observed completion of fusion in a cretaceous LVB sample. The black and dark grey regions are unfilled and resin filled pores or interparticle voids respectively while the light grey, largely featureless region is the fused vitrinite. Boundaries between bordering vitrinite macerals have disappeared and bridges connect well separated macerals. Devolatilization pores are the irregular sized, semicircular regions in the vitrinite macerals. A distinct inertite maceral, probably semi fusinite, is at the lower left border of the photo. Stress cracks arising during cooling are also visible.

Use of 1/4 λ plate with parallel polarizers permits the texture of the cooled molten phose and the semi coke to be observed. Figure 3 shows the texture of the anisotropy for 3 samples. Magnification of all samples is 200X. The uppermost figure shows elongated, flow domain texture at 458°C that is typical of both carboniferous and cretaceous LVB coals. Texture has been interpreted by Grint et al. [8]. Surprising is that this anisotropy is seen at a temperature 25°C below the temperature of maximum dilatation measured using a Ruhr dilatometer for the coal [4]. The coal must still be fluid at this temperature. Thus, the texture represents either structure in the softened or molten coal or formed as the coal solidifies on cooling in the sample preparation procedure. Appearance of anisotropy prior to the temperature of maximum dilatation, that is, while the coal was still plastic, occurred with both cretaceous and carboniferous MVB coals. It did not occur with the HVB samples.

For these coals, the temperature of maximum dilatation coincided with the temperature of the first appearance of anisotropy so that the latter temperature does signal semicoke formation for this rank of coal.

Coal rank (vitrinoid mean reflectance) affects texture of the semi coke strongly. Figure 3b shows well developed fine mosaic anisotropy surrounding a pore in the lower right of the photomicrograph. The vitrinoid material seems tightly bonded to the unsoftened and unfused semi fusinite that appears in the upper part of the photomicrograph. The coal used for this sample was a cretaceous HVB which had a reduced vitrinite content. The fine to coarse grain texture is typical for the HVB coals. The temperature reached at the point where the photomicrograph was taken was 550°C. The texture seen in Fig. 3b contrasts well with the texture for an LVB sample shown in Figure 3a.

Figure 3c is taken from another, as yet unpublished study of coal carbonization during co-processing of bitumen and coal [7]. The circular black region is a resin filled devolatilization pore surrounded by bitumen semicoke. Fused vitrinite is the bright region with very little texture. The photomicrograph suggests that neither the bitumen or the plastic coal are mutually soluble and the presence of bitumen does not interfere strongly with the fusion of vitrinite macerals.

Plastofrost Applications

The brief discussion of the photomicrograph indicates some of the applications of the Plastofrost technique: development of anisotropic texture as carbonization proceeds; measurement of the softening temperature, the plastic range and, for HVB coals, the resolidification temperature; and pore size, distribution and wall thickness. Beginning with Duever's study [3,9], the Waterloo Coal Research laboratory has applied the Plastofrost to three problems: 1) measuring the effect of metal salts on coal particle fusion during bitumen coal co processing, 2) assessing the accuracy of the dilatometric plastic range, and 3) exploration of the failure of rheological tests to predict the good coking performance of North American cretaceous coals.

In the first of the above three applications [10], two cretaceous and two carboniferous coals were used along with a heavy bitumen (vacuum bottoms). Plastofrost samples were prepared from the coals with 0, 5 and 20 wt% metal salts, the vacuum bottoms, and slurries of 30 wt% coal in the vacuum bottoms with metal salt levels of 0, 5 and 20 wt%. It was found that the salt delayed initial fusion of the coal grains and completion of fusion. The anisotropic texture of the semicoke was diminished by the salt. The presence of vacuum bottoms suppressed coal fusion, probably by physically separating the coal grains. Fusion is also slightly suppressed at 20 wt% additive; 5 wt% seemed to have little effect. Dissolution of vitrine in the bitumen was not observed. The coal and vacuum bottom phases carbonize separately yielding distinct, but well bonded semicokes. Anisotropic texture of the vacuum bottoms coke is strongly diminished by the presence of the finely ground coal. The micrographs suggest that the metal salt impregnated coals expel the salt on softening. This salt collects on the maceral surfaces and may physically interfere with the fusion process.

The second and third applications employed the same Plastofrost data taken with two suites of HVB to LVB coals of the carboniferous and cretaceous eras. The coals were split by gravimetric means into vitrinite enriched and depleted samples. In our study of dilatometry plastic ranges [11], it was found that the plastic range agrees well with the range obtained from the Plastofrost initial softening and first appearance of anisotropy temperatures for coals showing positive total dilatations and HVB coals with high vitrinite content. This is shown in Figure 4. With the exception of several HVB coals, the dilatometer seriously underestimates the plastic range of poorly or non-dilatating coals. The explanation

for this is that dilatometry does not correctly measure the softening temperature of many coals. Only with HVB coals do the estimates of initial softening temperature by the two techniques agree.

As discussed earlier, the Plastofrost estimate of the resolidificatian temperature (semicoke formation) is incorrect for MVB and LVB coals. Thus, that technique does not give the "real" plastic range. The best estimate seems to come from using the Plastofrost measurement of the initial fusion temperature and the dilatometer reading of the temperature of maximum dilatation.

The third Plastofrost application [4] investigated the observation [12,13] that rheological tests on certain bituminous coals of cretaceous origin indicate that the coals have poor coking quality eventhough commercial use and ASTM Sole Heated Oven tests show that these coals produce good quality coke. The Plastofrost observations indicate cretaceous bituminous coals exhibit all the carbonization stages seen in good coking coals. Temperatures of the carbonization stages do not differ greatly between the carboniferous and cretaceous coals as well. The plastic range of the latter coals is generally smaller for the LVB coals; the difference approaches 55°C. It was concluded that the problem with the rheological tests lies with the assumption that contraction and dilatation depend only on fluidity of the coal. These changes probably reflect the viscosity of the softening coal and the size and distribution of the inert macerals in the coal.

Three years experience with the Plastofrost technique indicate measurements are reproducible, provided the same observer makes the readings. However, sample preparation is slow and measurements have a subjective element because different observers obtain different stage temperatures from the same sample.

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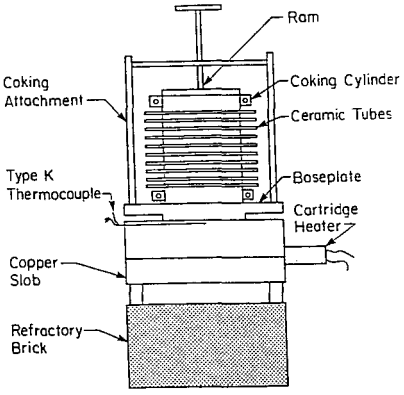

Figure 1 Schematic of the Plastofrost Apparatus

Figure 2 Completion of fusion (413°C) for a vitrinite enriched cretaceous LVB coal

(a) Flow domain anisotropy in a LVB Semicoke

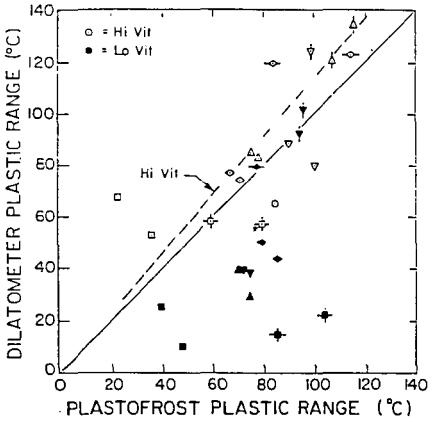

Figure 4 Cross plot of dilatometric and Plastofrost plastic ranges